

# **DIFFERENTIAL MOBILITY SPECTROMETRY: PRELIMINARY FINDINGS ON DETERMINATION OF FUNDAMENTAL CONSTANTS**

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## **Abstract**

The electron capture detector (ECD) has been used for 40+ years (1) to derive fundamental constants such as a compound's electron affinity. Given this historical perspective, it is not surprising that differential mobility spectrometry (DMS) might be used in a like manner.

This paper will present data from a gas chromatography (GC)-DMS instrument that illustrates the potential capability of this device to derive fundamental constants for electron-capturing compounds. Potential energy curves will be used to provide possible explanation of the data.

## **Introduction**

As the field strength (RF at constant temperature and pressure) is increased, the detector's response to a compound is expected to decrease. This decrease in signal occurs because of the greater diffusive losses as the ions are heated by the increasing RF field.

A Sionex brassboard system was used to assess the capability of a gas chromatography/differential mobility spectrometry (GC/DMS) to monitor spacecraft air. During this study, data was collected on the detector's response to NASA target compounds at various field strengths. The objective of this work was to determine if the dynamic range of the detector could be extended to higher concentrations by using the increased field strength to keep peak heights in range. As expected, the detector response to most compounds decreased with increasing field strength at 80°C (Figure 1). However, the data collected for dichloromethane (DCM) did not show a linear decrease in response with increasing field strength ( $\text{Townsend} = 10^{17} \times E/N$ ). On the contrary, the DCM response increased during a portion of the field strength ramp (Figure 2). In Figure 2, two runs, one month apart, illustrate that the observed trend was not an experimental artifact. The reactant ion peak (RIP) is shown for contrast. This paper will report on the results of the investigation to explain the DCM results.

## **Experimental**

The data shown in this paper was collected on a Sionex GC/DMS brassboard (Figure 3). Compound concentrations were generated from calibrated permeation tubes heated in a Kin-Tek gas generator. The lone exception was carbon tetrachloride ( $\text{CCl}_4$ ), which was made from serial dilutions of the neat liquid to a final mixture of trace level

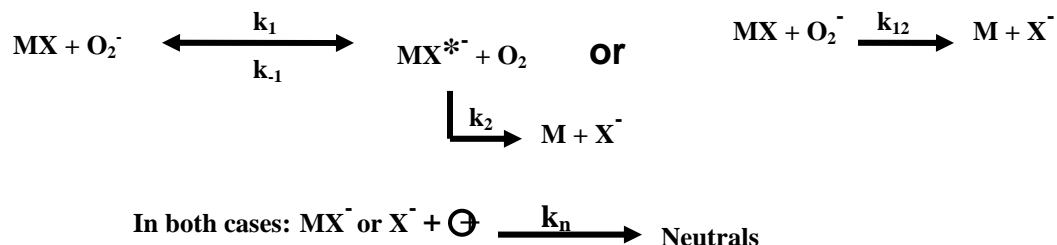
$\text{CCl}_4$  in a 6-liter summa-treated grab sample canister (GSC) with the balance being certified zero air. Streams from the Kin-Tek oven were merged and passed through a sampling tee (Figure 3) where the instrument acquired a sample perpendicular to the flow from the Kin-Tek. Typical merged flows from the Kin-Tek were 900 ml/min and the brassboard's pump sampled at 55 ml/min. Samples of  $\text{CCl}_4$  were obtained using a 2-liter sample bag (filled from the GSC) that connected to the brassboard's sample line (replaced the sampling tee).

The brassboard system acquired sample volumes of 13.75 ml (15 sec sampling time), which flowed through a preconcentrator containing Carboxen 569 (~ 3 mg) and Carbotrap B (~11 mg). The preconcentrator was desorbed at 300°C and the gas chromatograph (GC) retention times for analytes reported in this paper were less than 2 minutes on Restek's RTX-200 column (5 m x 0.18 mm). The GC column flow was approximately 1.5 ml/min and the make-up flow in the detector was 395 ml/min.

## Results and Discussion

It is postulated that the increased DCM response at higher field strengths is related to a change in the pathway of negative ion formation. DCM undergoes dissociative electron capture (Equation 1), but this requires activation energy for the ionization to occur (3). The two mechanisms shown below can not be distinguished using nominal electron capture detector (ECD) data (3).

Equation 1:



The required activation energy means that DCM does not attach thermal electrons at the maximum rate, thus making it a weak responder in low temperature ECD. Increasing the temperature of the ECD enhanced the DCM response as more molecules achieve the energy required to attach electrons.

In Figure 4 it is clear that the detector response to DCM increases as the temperature of the detector is elevated. At any fixed field strength, the detector response to DCM increased as a function of the detector temperature. This is easily explained by the higher temperature in the ionization region. As in the ECD, the higher temperatures provide the necessary activation energy to ionize more DCM molecules, which increases detector response. This enhanced response with elevated temperature was expected based upon ECD data. However, at a fixed temperature the increased response to DCM

at approximately 110 Tds was unexpected and definitely a phenomenon related to the applied fields in the DMS rather than a process in the ionization region. There should have been a steady decrease in peak height with increasing field strength.

Kinetic models of the electron capture mechanisms have been developed and the Arrhenius plot of  $\ln KT^{3/2}$  vs.  $1/T$  has been used to derive activation energies and electron affinities from experimental data (4). It was assumed that equilibrium was achieved between applications of the RF field; hence experimental DMS data could be used to obtain “K”. The DMS data was used to arrive at K in two ways: the corrected DCM peak height (average spectral noise subtracted from the DCM peak) and Equation 2. In this case “b” was the RIP height in the absence of the analyte and “e” was the RIP peak height with the analyte present. This equation has been used for plots of ECD data.

$$b^2 - e^2 / be = KT \quad \text{Eq 2}$$

The current data is plotted in Figure 5, along with ECD data (5). The intercepts are very close for the DMS peak height data and the ECD data, but the plot of equation 2 data resulted in a lower intercept. The activation energy can be determined from the slopes. The activation energy was calculated to be 0.37 eV from the ECD data; whereas the calculated value for the DMS data was 0.25 eV for both methods (with 140°C data point removed from Equation 2 method). The activation energy for the RIP ( $O_2^-$ ) was determined to be 0.06 eV, which would bring the DCM activation energy to about 0.31 eV for the DMS data. This is still slightly lower than the ECD (electron attachment) data.

The different values for the activation energy (slopes) can be explained in two ways. First, the gas flow into the ECD is usually an inert gas plus a small amount of methane; therefore ionization is by attachment of the electrons (thermalized by the methane) to the molecules. However, in the GC/DMS brassboard the detector gas flow is air, so ionization occurs via charge transfer from  $O_2^-$  to the molecule. The mechanisms and energies required for ionization via  $O_2^-$  will be different than those for thermalized electrons (ECD). Secondly, the maximum peak height at each temperature corresponded to roughly the same field strength, which indicates that perhaps a change has occurred in the dissociative pathway. Potential energy curves, using a modified Morse potential have been drawn for dichloromethane that propose four dissociative paths (5). In Figure 6, the molecular and four ionic Morse potential energy curves are shown for dichloromethane, plus the energy distribution for the nominal pathway. The DMS may be explained as a transition to a potential energy curve in an excited state (dotted potential energy curve), which would fit with the smaller activation energy obtained from the DMS data.

As opposed to dichloromethane, carbon tetrachloride has little or no activation energy for dissociative electron capture; hence it exhibits the maximum electron capture rate even at low detector temperatures. Theoretically, this means that the detector response to  $CCl_4$  should decrease with peak height as observed with ethanol and xylene. It is seen in Figure 7a that the  $CCl_4$  peak height seems to be declining, but again at higher field strengths a slight increase in peak height is observed. The scale of the y-axis is the same for Figures 4 and 7a and this shows that the  $CCl_4$  peak height increase was not

nearly as pronounced as the DCM change. Nevertheless, the increase was clearly present and the data was reproducible. It should be noted that the field strength for the  $\text{CCl}_4$  peak maximum is very close to the one identified for DCM. Again the evidence seems to point to ionization occurring via a different potential energy curve. The potential energy curves for  $\text{CCl}_4$  (5) are shown in Figure 7b and it appears one of the two “backside” curves (plots with triangles and squares) might be responsible for the observed phenomena. Unfortunately, data for  $\text{CCl}_4$  was collected at only one detector temperature, so it is impossible to speculate further on the mechanism of ionization or to derive the activation energy.

## Conclusion

A routine investigation of a GC/DMS system’s performance discovered unexpected results in the detector’s negative mode response to chlorinated alkanes. This led to a more thorough characterization of the detector’s response to dichloromethane at increasingly higher detector temperatures. Data from the DCM study were used to derive activation energies for the ionization of DCM and potential energy curves were used to propose explanations for the increased peak heights observed at higher field strengths. Most importantly, this work has shown that even fine “structure” in the data, such as seen for carbon tetrachloride, may provide clues to the processes occurring in the DMS detector.

## References

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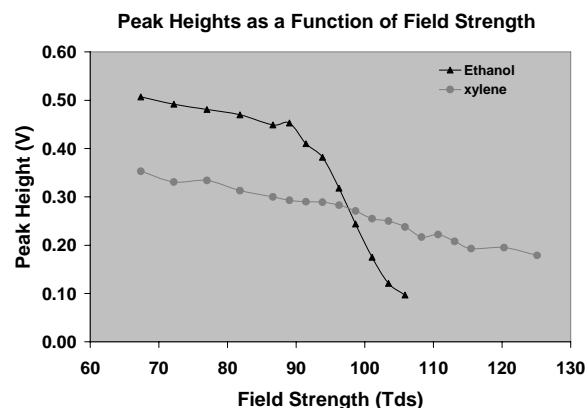


Figure 1 Plot of ethanol and xylene peak heights as the DMS field strength (Townsend) is increased.

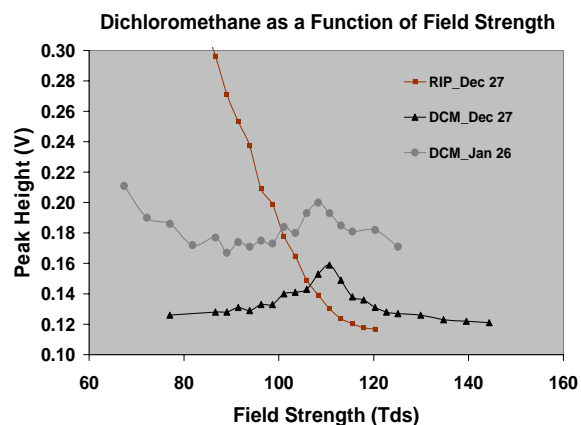


Figure 2 Dichloromethane (DCM) peak height versus field strength (Townsend) and RIP peak height versus field strength

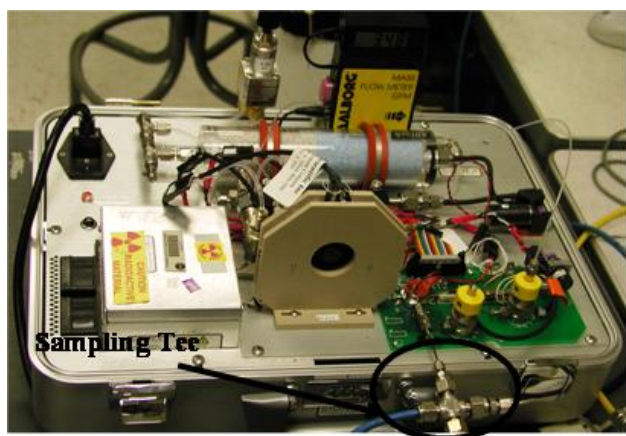


Figure 3 Sionex GC/DMS Brassboard . The beige octagon holds the GC column and the silver box at the lower left corner contains the DMS detector.

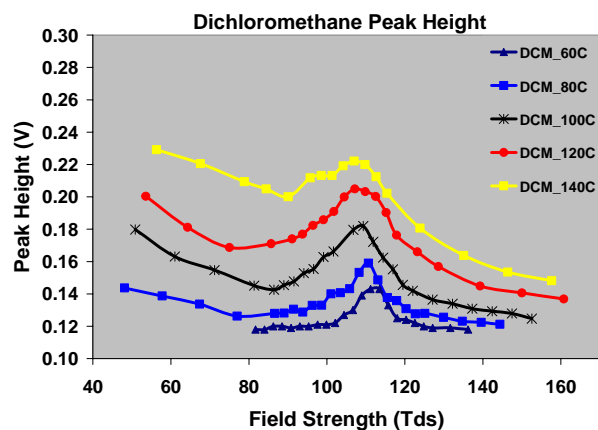


Figure 4 The peak height for dichloromethane is shown to increase at any field strength as the detector temperature is increased.

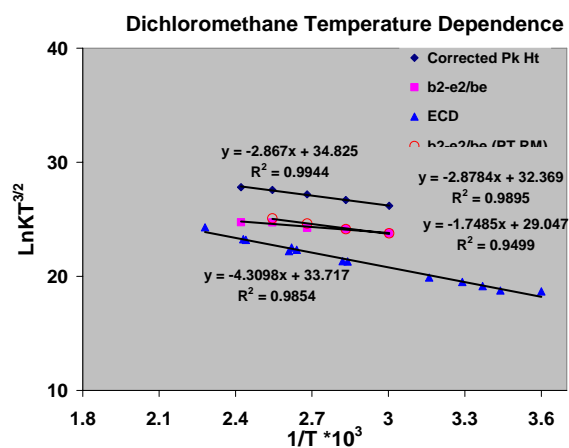


Figure 5 Dichloromethane temperature dependence in DMS compared to ECD

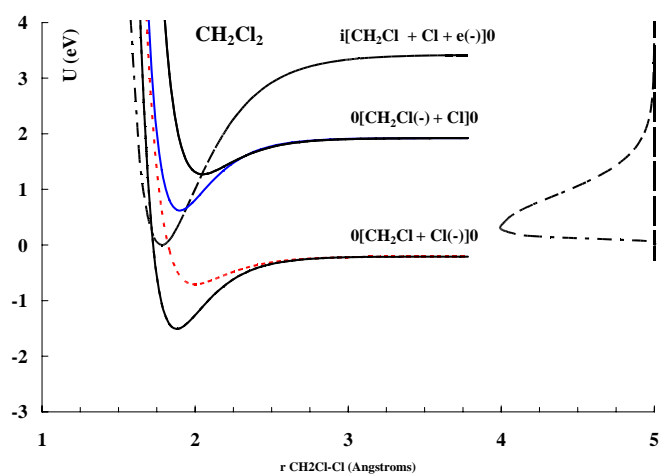


Figure 6 Potential energy curves for dichloromethane using a modified Morse potential

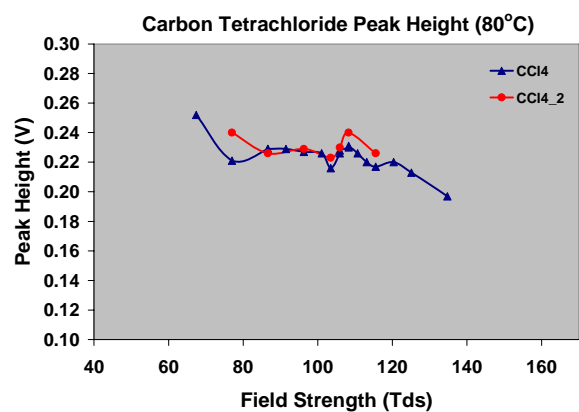


Figure 7a DMS detector response to carbon tetrachloride with increasing field strength. The CCl4\_2 data was obtained with the same parameters as the CCl4 data, but the concentration of the former was slightly higher.

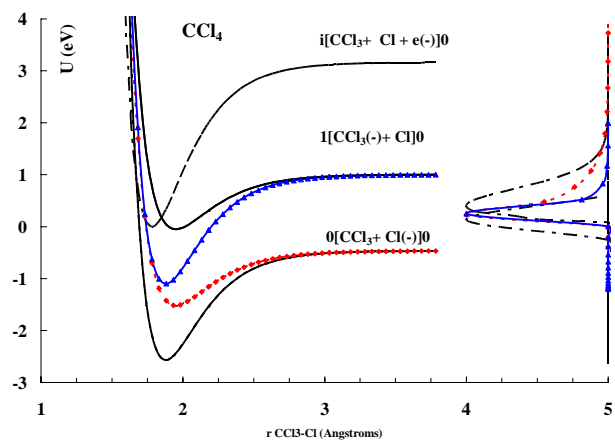


Figure 7a Potential energy curves for carbon tetrachloride